# TEST PLAN FOR RECLAIMED PETROLEUM HYDROCARBONS

Submitted to the US EPA

by

The American Petroleum Institute Petroleum HPV Testing Group

**Consortium Registration #** 

### RECLAIMED PETROLEUM HYDROCARBONS TEST PLAN

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#### **PLAIN LANGUAGE SUMMARY**

The five high production volume (HPV) substances contained in this test plan are all petroleum hydrocarbon mixtures (oils) that are produced as byproducts in petroleum refineries. They are often referred to as slop oils. Some of the slop oils are skimmed from process waters or wastewater treatment plants and some are recovered from spills or the washing of equipment. Whenever possible, these oils are returned to the refinery to be made into petroleum products. Because the source and composition of these oils varies, the chemical definitions given to these substances are very general. Because they are not intentionally manufactured and come from many parts of the refinery, the slop oils are made up of an almost infinite combination of petroleum hydrocarbons and water. Therefore, it is not possible to select a slop oil that would be considered representative of any of the substances covered in this test plan. Because all of the hydrocarbon components in these materials are being addressed in other test plans on petroleumderived products or streams, the Testing Group expects that the overall hazard of any specific slop oil can be predicted based on its composition and the toxicity characteristics of its petroleum components. The Testing Group is proposing no health or environmental effects testing of these materials.

#### DESCRIPTION OF RECLAIMED PETROLEUM HYDROCARBONS

The refining of crude oil into petroleum products uses distillation and a variety of other chemical conversion processes to separate and combine the basic types of hydrocarbon molecules into petroleum "streams" which have the characteristics needed for blending commercial petroleum products. As is the case for many industrial processes, the refining of petroleum products produces a number of unintentional byproducts, wastes, and other oil-containing process streams that are not typically sold as products. These materials are "reclaimed" and recycled into the refining process to be processed into finished products.

All of the substances contained in this test plan are byproducts derived from the refining of petroleum crude oils, that is, they are not intentionally manufactured for introduction into commerce. For example, oil is recovered from process water streams, from sewers or storm drains and from wastewater treatment plants by skimming and other mechanical separation methods. In addition, catalysts, filters and other process materials in contact with oil are washed to recover hydrocarbons. Oil that is spilled or makes its way to wastewater treatment plants is recovered, and whenever possible, is recycled back into the refinery.

Because of the compositional variability inherent in the processing of petroleum materials, the definitions developed for the CAS numbers for reclaimed petroleum hydrocarbons are written in broad, general terms. Therefore, the CAS descriptions are

not useful in determining the exact composition of any specific reclaimed petroleum substance. Furthermore, because of the qualitative nature of these CAS descriptions, there may be significant compositional overlap between two substances with different CAS numbers. A brief description and discussion of each substance follows:

<u>Wastes, petroleum</u> <u>CASRN 68477-26-9</u> - The waste products from any petroleum refinery or production process which has been dewatered. It is commonly called slop oil.

This CASRN is used to describe any petroleum waste which has been dewatered. It can range from lighter hydrocarbons derived from fuel manufacturing processes to heavier materials from lube manufacturing. All but the heavier, sediment containing oils are typically recycled and refined into petroleum products.

#### Petroleum products, C5-12, reclaimed, wastewater treatment CASRN 68956-70-7

A complex combination of hydrocarbons recovered in a dilute solution from a wastewater treatment plant. It consists of hydrocarbons having carbon numbers predominantly in the range of C5 through C12.

This material represents the lighter hydrocarbons that are skimmed from the surface of water present in wastewater treatment plants. Oil skimmed from wastewater is typically transferred to tanks where further water separation occurs. The oil fraction is introduced back into the refinery. Since the wastewater can come from many different parts of the refinery, the exact carbon range and hydrocarbon types that are present in any one oil mixture is highly variable and dependent on the crude source and the refining processes that the hydrocarbon streams had undergone.

<u>Hydrocarbons, C>=20, petroleum wastes</u> <u>CASRN 68476-53-9</u> - A complex combination of hydrocarbons produced as waste material from slop oil, sediments, and water. It consists of hydrocarbons having a carbon number predominantly greater than C20 and boiling above approximately  $350^{\circ}$ C ( $662^{\circ}$ F).

This material represents the heavier hydrocarbons recovered from wastewater treatment plants or present in other oil/water mixtures or tank bottom sludges. Such mixtures are typically dewatered and further separated by mechanical means to recover as much oil as possible. The oil fraction is returned to the refinery. Sediment containing sludges are typically disposed of as wastes. Since the slop oils from which these oils are recovered can come from many parts of the refinery, their composition is highly variable and dependent on the crude source and the refining processes that the oils have undergone.

#### Residues (petroleum), clay-treating filter wash CASRN 68918-73-0

A complex residuum from the solvent washing of clay-treating filters. It consists predominantly of unsaturated hydrocarbons having carbon numbers predominantly greater than C20 and boiling above approximately 350°C (662°F).

Clay filtering is a finishing step used to improve the stability and color of lubricating base oils by removing higher molecular weight aromatics, olefins and other more polar

hydrocarbons. Improvements in solvent extraction procedures and the increased use of hydrofinishing processes have largely replaced the use of clay filtering. Materials adsorbed by the clay are backwashed with a solvent to regenerate the filter. The residual hydrocarbon from this wash is typically disposed of as a waste. The composition is highly variable and dependent on the crude source and the method of solvent refining used to treat the base oils prior to filtering.

<u>Fuel oil, residual, wastewater skimmings</u> <u>CASRN 68956-48-9 -</u> The recovered oil obtained by skimming all plant oil-bearing water streams. It consists predominantly of hydrocarbons having carbon numbers predominantly in the range of C7 through C10.

Because all of the hydrocarbons in this material are lighter, they are either reintroduced into the refinery or burned as fuel in the refinery.

## THE HAZARDS OF THE HYDROCARBONS CONTAINED IN RECLAIMED OILS ARE ADDRESSED IN OTHER PETROLEUM PRODUCT TEST PLANS

The Petroleum HPV Testing Group has submitted test plans for eleven product groups (see Table 1). These test plans address nearly 400 different petroleum products and intermediate processing streams that encompass a wide range of carbon numbers and classes (the Table indicates the approximate carbon range of the substances in each product grouping). While these products and streams are all complex mixtures, the CAS definitions provide some understanding of their likely composition by indicating chemical processing and approximate carbon and boiling ranges.

That is not the case for the reclaimed hydrocarbon substances presented in this test plan. While some of the definitions indicate carbon number or boiling range, only one indicates process (clay treating), and clay treating can be used for many different feed stocks. The reason that reclaimed hydrocarbons cannot be characterized chemically with any degree of certainty is that a slop oil, or oil skimmed from wastewater can come from any number of different processes, and in fact, it is common practice to combine oil-bearing water streams from different parts of the refinery for separation. Therefore, the composition of slop oils can vary from day to day depending on where they are collected, and it is not known what hydrocarbon species might be present in any given slop oil.

All the reclaimed oils described in this plan are composed of varying ratios of materials (hydrocarbon types) that are being characterized in other petroleum product test plans. These ratios can vary depending on process from which the oil is recovered, mixing of wastes from different processes, etc. In fact, all the hydrocarbon species that could possibly be present in reclaimed oils are also present in the substances being addressed in the other eleven test plans for petroleum products. And if the need arises, it is possible to chemically analyze any slop oil produced at a refinery, and if it has a carbon range in the diesel fuel range, or perhaps heavier like lube oils, information generated in the test plans for diesel fuels or lube oils would be relevant to those materials. Note in Figure 1 that the substances covered by petroleum product test plans span the whole range of carbon

numbers contained in crude oil, from the lighter gases to heavier solid materials such as asphalt and coke.

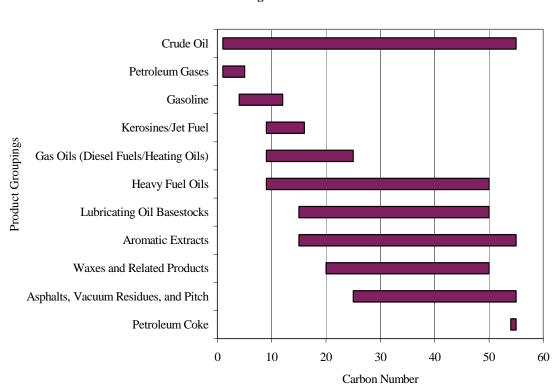


Figure 1.

From a practical standpoint, the Testing Group does not believe that slop oils represent a significant hazard. The potential for exposure to these materials is very low and confined to persons working in petroleum refineries. They represent only a tiny fraction of the materials handled at petroleum refineries and are only produced in "high volumes" because of the large amounts of petroleum refined. Since there is a significant financial incentive to recover usable hydrocarbons, a substantial portion of slop oils are reintroduced into the refinery and refined into petroleum products. Those that cannot be recycled are disposed of as wastes. In this sense, they can be viewed as isolated intermediates in the production of the petroleum products and streams covered by the other HPV categories.

In summary, the Testing Group believes additional efforts to characterize the hazards of slop oils are not warranted. They represent byproducts in the refining of petroleum products that are not introduced into commerce, and that are recycled into the refining process to the greatest extent possible. More importantly, they consist of varying ratios of the same hydrocarbons being addressed in other petroleum product test plans. Consequently, if it becomes necessary to characterize the hazards of a particular slop oil, the data being generated in the other petroleum product test plans will provide adequate information to assess the potential hazard of these substances.